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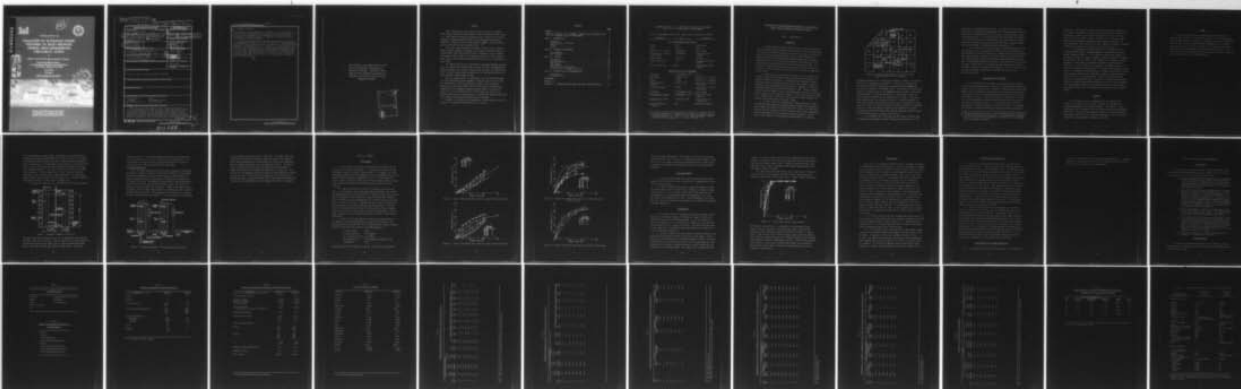
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EVALUATION OF ULTRAVIOLET/OZONE TREATMENT OF ROCKY MOUNTAIN ARS--ETC(U)  
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TECHNICAL REPORT Y-78-1

# EVALUATION OF ULTRAVIOLET/OZONE TREATMENT OF ROCKY MOUNTAIN ARSENAL (RMA) GROUNDWATER (TREATABILITY STUDY)

by

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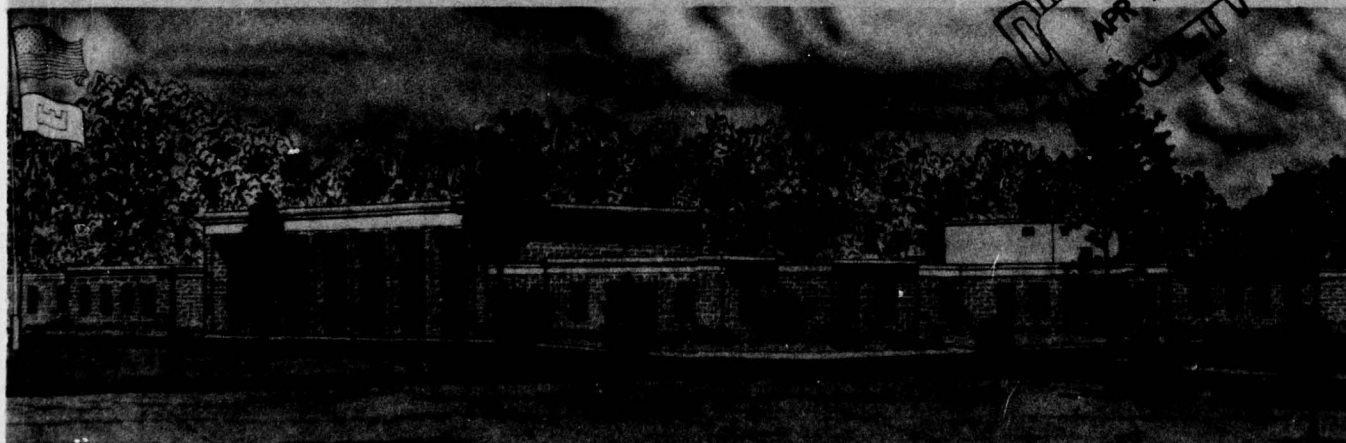
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20. ABSTRACT (Continued).

The groundwater at RMA is known to be contaminated with chlorinated hydrocarbons, organophosphorous, organosulfur, and other organic compounds. The purpose of this investigation was to determine the feasibility of using ultraviolet/ozone (UV/O<sub>3</sub>) treatment to reduce the concentration of those contaminants in the RMA groundwater.

This report discusses the experimental results obtained from treating RMA groundwater with UV light and ozone. The laboratory investigations used two different batch reactors and varied such parameters as ozone concentration, temperature, and wattage of UV light. Continuous flow experiments were also conducted. In batch experiments, total organic carbon removal ranged from 40 to 90 percent. The concentrations of diisopropylmethylphosphonate (DIMP) and other organic compounds were significantly reduced. In the continuous flow phase of the study, it was possible to remove 93 percent of the DIMP originally present and lower the levels of all other organic contaminants to below detectable limits.

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## PREFACE

This investigation was conducted during the period 6 December 1976-31 March 1977 by the Environmental Effects Laboratory (EEL) of the U. S. Army Engineer Waterways Experiment Station (WES) for the Project Manager for Chemical Demilitarization and Installation Restoration (PM-CDIR). Funding for this study (Task No. 011800) was authorized by IAO No. CDIR 3-77, dated 17 November 1976.

This report was prepared by LT Robert E. Buhts, CE, Dr. Philip G. Malone, and Mr. Douglas W. Thompson, the Treatment Processes Research Branch (TPRB), EEL, WES, under the direct supervision of Mr. Norman R. Francingues, Chief, TPRB, and the general supervision of Mr. Andrew J. Green, Chief, Environmental Engineering Division, and Dr. John Harrison, Chief, EEL.

The bench-scale tests were performed by Westgate Research Corporation, Los Angeles, California, under contract No. DACW 39-77-M-0858 and Houston Research, Inc., Houston, Texas, under contract No. DACW 39-77-M-0753. Chemical analyses were conducted by the contractors and also by Rocky Mountain Arsenal (RMA) and WES.

Special acknowledgement is extended to the following individuals for their assistance and encouragement during the course of this work: Drs. Michael Witt and Nicolay Timofeeff, Messrs. Brian Anderson, Ed Berry, and Carl Loven (RMA); CPT Joe Kolmer and Mr. Dennis Wynne (PM-CDIR); Mr. Don Campbell, Edgewood Arsenal (EWA); LTC Charles H. Coates, Jr., CE, CPT Terry Hand, CE, LT Ash Kahn, CE, and Mr. Jack Dildine (WES); and also the personnel of the Material Analysis Laboratory Group (RMA) and the Analytical Laboratory Group (WES).

Director of WES during the preparation of this report was COL J. L. Cannon, CE. Technical Director was Mr. F. R. Brown.

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CONVERSION FACTORS, U. S. CUSTOMARY TO METRIC (SI) AND METRIC  
(SI) TO U. S. CUSTOMARY UNITS OF MEASUREMENT

Units of measurement used in this report can be converted as follows:

<u>Multiply</u>	<u>By</u>	<u>To Obtain</u>
<u>U. S. Customary to Metric (SI)</u>		
inches	25.4	millimetres
feet	0.3048	metres
gallons (U. S. liquid)	0.003785412	cubic metres
gallons (U. S. liquid) per minute	0.003785412	cubic metres per minute
pounds (mass)	0.4535924	kilograms
parts per million	1.0	milligrams per cubic metre
parts per billion	1000.0	milligrams per cubic metre
<u>Metric (SI) to U. S. Customary</u>		
nanometres	$0.003280839 \times 10^{-6}$	feet
millilitres	$0.2642 \times 10^{-3}$	gallons (U. S. liquid)
litres	0.2642	gallons (U. S. liquid)
millilitres per minute	$0.2642 \times 10^{-3}$	gallons (U. S. liquid) per minute
litres per minute	0.2642	gallons (U. S. liquid) per minute
milligrams	$0.002204622 \times 10^{-3}$	pounds (mass)
milligrams per minute	$0.002204622 \times 10^{-3}$	pounds (mass) per minute
milligrams per litre	$6.242797 \times 10^{-5}$	pounds (mass) per cubic foot
Celsius degrees or Kelvins	9/5	Fahrenheit degrees*

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\* To obtain Fahrenheit (F) readings from Celsius (C) readings, use the following equation:  $F = 9/5(C) + 32$ . To obtain Fahrenheit readings from Kelvin (K) readings, use:  $F = 9/5(K - 273.15) + 32$ .



EVALUATION OF ULTRAVIOLET/OZONE TREATMENT OF ROCKY MOUNTAIN  
ARSENAL (RMA) GROUNDWATER (TREATABILITY STUDY)

PART I: INTRODUCTION

Background

1. Rocky Mountain Arsenal (RMA) has been a chemical manufacturing and chemical demilitarization facility since 1942. Military operations have included the production of GB nerve gas, lewisite, mustard, arsenic chloride, and chlorine gas, as well as the fabrication of munitions containing white phosphorous and chemical warfare agents. Demilitarization of GB munitions and mustard-filled munitions, along with hydrazine blending, have been additional missions of RMA. In addition to these military operations, private corporations have and continue to operate industrial facilities for production of pesticides on this site.

2. Wastes from various chemical processes were discharged into unlined basins until an asphalt-lined evaporation lake designed for complete retention (Reservoir F in Figure 1) was completed in 1955.<sup>1</sup> Repeated contact of rainwater and groundwater with chemical wastes in and beneath the unlined basins has resulted in transport of chemical compounds within and outside the boundaries of RMA. Recent studies<sup>2</sup> indicate that the asphalt liner of the evaporation lake and the chemical sewers leading to the lake may be leaking. Further indications are that all of these sources contribute to the pollution plumes presently migrating towards the northern boundary of RMA.

3. In April 1975, the Colorado State Health Department (CSHD) informed RMA that diisopropylmethylphosphonate (DIMP) and dicyclopentadiene (DCPD) were present in the aquifer north of RMA. The CSHD also directed that all possible efforts be made to remove these contaminants from the groundwater flowing across the arsenal boundary. Initial efforts were directed at determining the applicability of selected

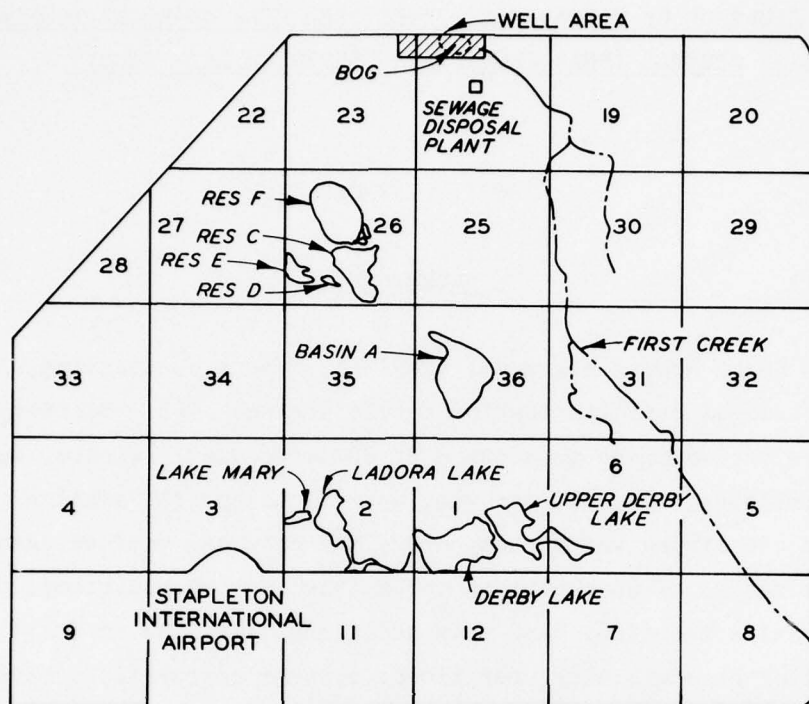


Figure 1. General groundwater well location, Rocky Mountain Arsenal, Denver, Colorado

treatment processes such as adsorption, chemical oxidation, and reverse osmosis, for treating this wastewater. This work was initiated by the Mobility Equipment Research and Development Command (MERADCOM), Ft. Belvoir, Virginia, in September 1975.<sup>3</sup> Concurrent with treatability studies of surface water at RMA, MERADCOM funded a study<sup>4</sup> to establish the feasibility of oxidative destruction of pesticides in water by ozone acting in combination with ultraviolet (UV) light. Five pesticides were selected for evaluation (Table 1). Aqueous solutions of each pesticide were subjected to UV/ozone (UV/O<sub>3</sub>) photochemical oxidation. The results of this work showed the UV/O<sub>3</sub> process to be extremely effective. The investigators stated that the pesticides and their intermediate oxidation products were rapidly destroyed, with all carbon in the molecules going to carbon dioxide (CO<sub>2</sub>).

4. In September 1976, Mill, Epstein, and Schiff<sup>5</sup> reported that UV combined with hydrogen peroxide (UV/H<sub>2</sub>O<sub>2</sub>) proved effective in the

destruction of organophosphorous wastes. As reported in this work, solutions of isopropylmethylphosphonate (IMP) and methylphosphonic acid (MPA) were considered successfully oxidized to carbon dioxide, water, and phosphoric acid. Other investigators have discovered that UV/H<sub>2</sub>O<sub>2</sub> is also an effective and efficient method for treating water contaminated with explosives such as trinitrotoluene (TNT), cyclonite (RDX), homocyclonite (HMX), and ammonium picrate (Explosive D).<sup>6</sup>

5. In a more recent study conducted on pink water obtained from the Burlington, Iowa, Army Ammunition Depot, the UV/O<sub>3</sub> treatment was demonstrated to be equally effective in treating effluents contaminated with explosive waste compounds.\* The pink water (containing TNT, RDX, etc.) was processed through a 25-gal,\*\* continuous-flow, UV/O<sub>3</sub> pilot unit. Using 18-mg ozone/mg total organic carbon (TOC) and low-intensity UV light, the TOC level of the pink water was reduced from 15 ppm to less than 1 ppm with a contact time of 86 min. In all of these studies, the use of UV light significantly increased the rate of ozone or peroxide oxidation.

#### Applicability of UV/Ozone

6. The utilization of UV light to enhance the ozone oxidation process is a useful application of theory. A photochemical reaction is unique in that it deals with the interaction between light and molecules. Because of this interaction, reactions of electronically excited molecules usually occur from completely different energy levels than those encountered in thermal or ground state systems. Absorption of radiation is a simple process but once having occurred places the excited molecule in a complex situation. It is now faced with a variety of photophysical processes by which it can either return to its original ground state or undergo photochemical changes resulting in molecular

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\* Personal communication with J. Zeff, Westgate Research Corporation.

\*\* A table of factors for converting U. S. customary units of measurement to metric (SI) units and metric (SI) units to U. S. customary units is presented on page 4.

alteration. Introduction of ozone (itself electronically unstable) to the molecular environment at this point offers immediate resolution of the problem. Chemical bonds break and reform as the ozone and electronically excited organic species combine to form an excited intermediate, which undergoes cleavage to yield simpler compounds. The UV/O<sub>3</sub> process may then repeat itself until compounds incapable of further oxidation are formed (e.g., CO<sub>2</sub>, H<sub>2</sub>O, Cl<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, SO<sub>4</sub><sup>2-</sup>, etc).

7. The groundwater at RMA is known to be contaminated with chlorinated hydrocarbons, organophosphorous, organosulfur, and other organic compounds (Table 2). The identified contaminants present in the water crossing the northern boundary of RMA are difficult to degrade biologically. They do, however, lend themselves to removal by carbon adsorption. This method of treatment succeeds in transferring contaminants to a solid adsorbant and produces a secondary problem, i.e., the need to reclaim and/or dispose of a relatively large amount of spent carbon. A preferable treatment method, if proved cost-effective, is one that completely destroys the undesirable chemical compounds and generates little or no secondary waste. Theoretically, photochemical oxidation can perform this task. Since some of these compounds absorb UV light resulting in molecular alteration, it was felt that a combined UV/O<sub>3</sub> photochemical oxidation water treatment process could successfully reduce their level of concentration and perhaps effect complete removal.

#### Purpose

8. The purpose of this investigation was to determine the feasibility of using UV/O<sub>3</sub> treatment to reduce the concentration of selected contaminants in the RMA groundwater. The results of this investigation may be compared with data obtained from carbon adsorption studies being performed concurrently on samples of similar groundwater. These bench studies provide a basis for conducting a pilot plant scale investigation of groundwater treatment at the RMA.



### Scope

9. This report describes a two-phase concentrated effort to establish the feasibility of using UV/O<sub>3</sub> systems to treat the ground-water at RMA. Phase I consisted of a laboratory evaluation using batch reactors, various ozone concentrations, temperatures, and different wattages of UV light. Phase II consisted of a limited continuous flow study based on the experimental results obtained from Phase I. The continuous tests were designed to ascertain dynamic operating conditions and overall efficiency of a multistage unit.

PART II: SAMPLES AND EQUIPMENT

Test Samples

10. Groundwater (550 gal) was obtained from two wells along the northern boundary of RMA (Figure 2). Pump wells (PW) No. 2 and

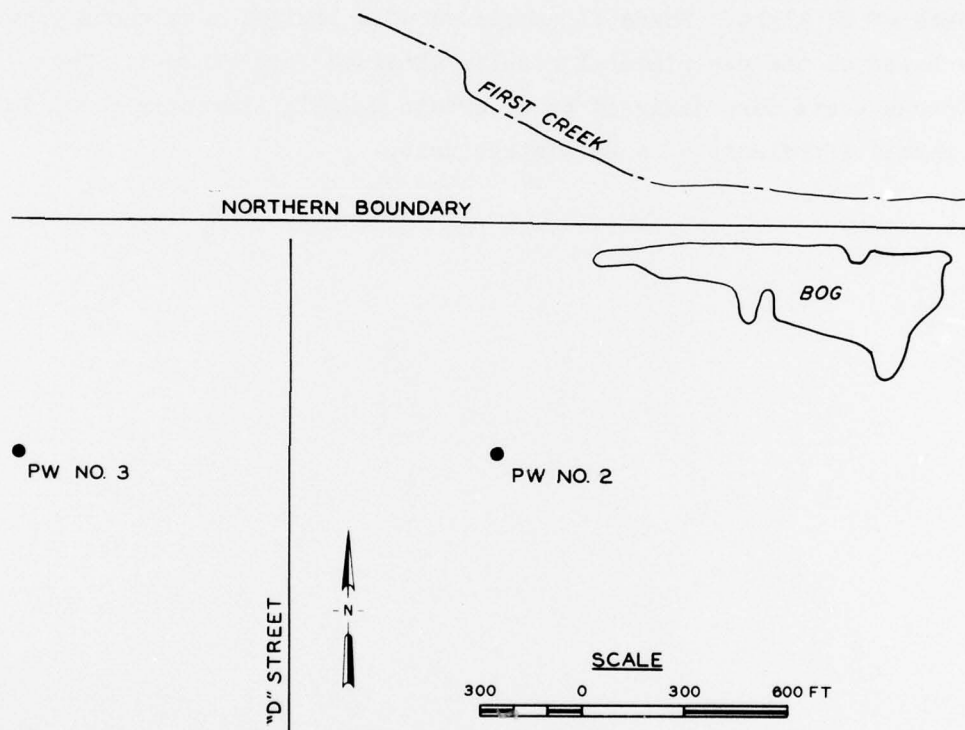


Figure 2. Location of the sampled pump wells (PW) within the well area

No. 3 were selected because of their alignment with a proposed interim groundwater containment system. Gas chromatographic analysis showed each well to have high concentrations of organic compounds (Table 3). In addition to the determination of organic constituents, a thorough chemical analysis was performed on water from each well. This characterization included determining most of the general parameters used for water-quality evaluation (Table 4) and conducting metals analysis (Table 5).

11. Equal volumes of the two water samples were mixed and

allowed to come to equilibrium, resulting in a composite representative of groundwater from the RMA northern boundary. This mixture was filtered and used as a feedstock in all of the experimental runs. For comparative analysis, public water supply criteria are given in Appendix A.

### Test Equipment

#### Batch tests

12. The UV/O<sub>3</sub> batch experiments were conducted in two different reaction vessels. Reactor A (Figure 3) is a 12-l, 6-in.-diam,

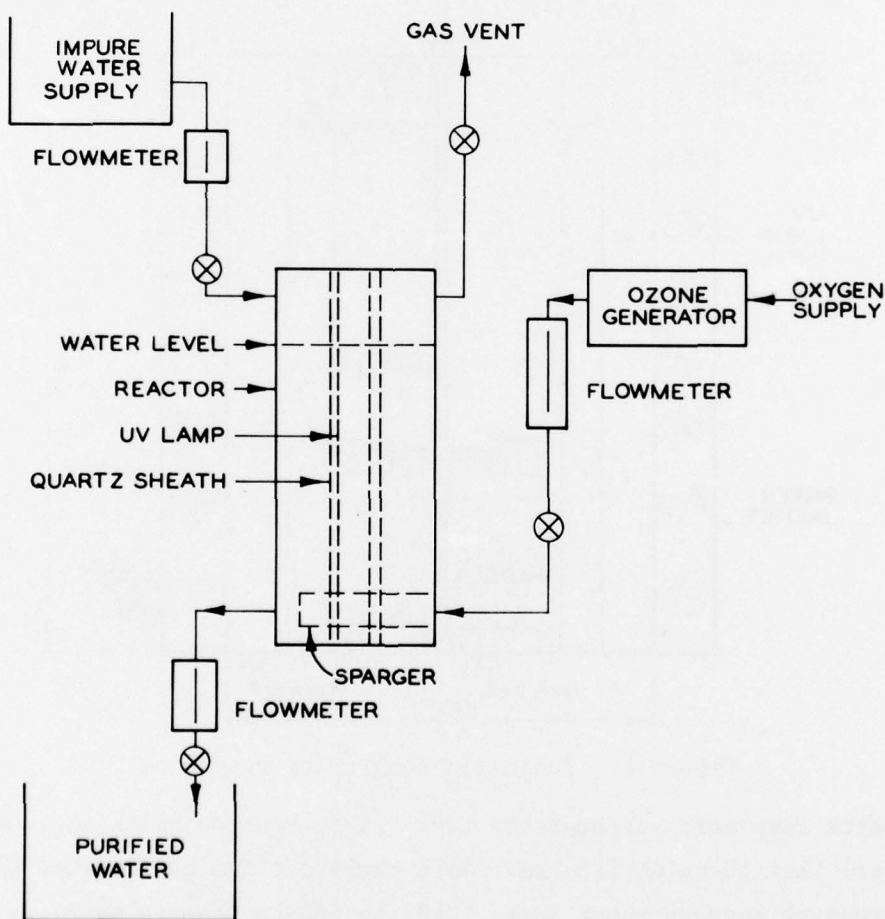


Figure 3. Schematic diagram of reactor A

30-in.-high stainless steel system, containing two 1-in.-diam, porous aluminum gas spargers approximately 2 in. above the base of the reactor. A low-pressure, mercury vapor lamp (240- to 260-nm primary wavelength band) is housed in a 1-in.-diam quartz tube located on the vertical axis of the reactor. The necessary lamp voltage was provided by a mercury lamp ballast/transformer. Ozone was produced by an OREC, model 03B20 ozone generator. Its rated capacity is 2 lb of ozone per day from oxygen feed. The concentration of ozone produced in the oxygen-ozone ( $O_2/O_3$ ) mixture can be varied over the range of 0.5-4 percent by weight by changing the ratio of power input to oxygen flow.

13. Reactor B (Figure 4) is a 21-l stainless steel system having

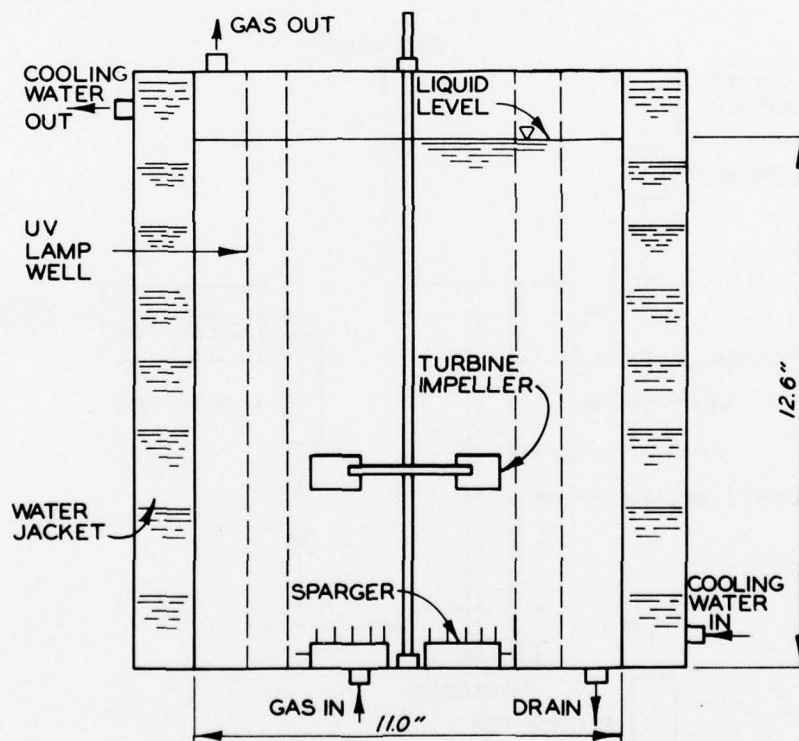


Figure 4. Schematic diagram of reactor B

two quartz lamp wells through the top. It is equipped with an impeller (stirrer) that turns at 515 rpm. Into the wells can be inserted Hanovia high-pressure mercury vapor lamps (240- to 260-nm primary wavelength band). Each lamp is completely below the liquid level. Ozone was



produced from a W. R. Grace and Company model LG-2-L2 ozone generator. Its rated capacity is 2.5 lb of ozone per day from oxygen feed. The concentration of ozone in the  $O_2/O_3$  mixture being fed to the reactor can be varied over the range 0.5-10 percent by weight.

#### Continuous flow tests

14. The  $UV/O_3$  continuous flow tests were conducted by connecting two reactor A stages in series. The start-up procedure for this system consisted of pumping 12 l of water into stage one, activating the UV lamp, and sparging with an  $O_2/O_3$  mixture of known ozone concentration at a preset flow rate. The reactor was then run as a batch system until a desired level of TOC was attained (usually 5 ppm). The contents of stage one were then pumped into stage two. Stage one was again filled with water, and both stages were operated in a batch mode until 5-ppm TOC was obtained in stage two. The system was then converted to a counter-current, continuous flow mode (Figure 5). As illustrated in the diagram,

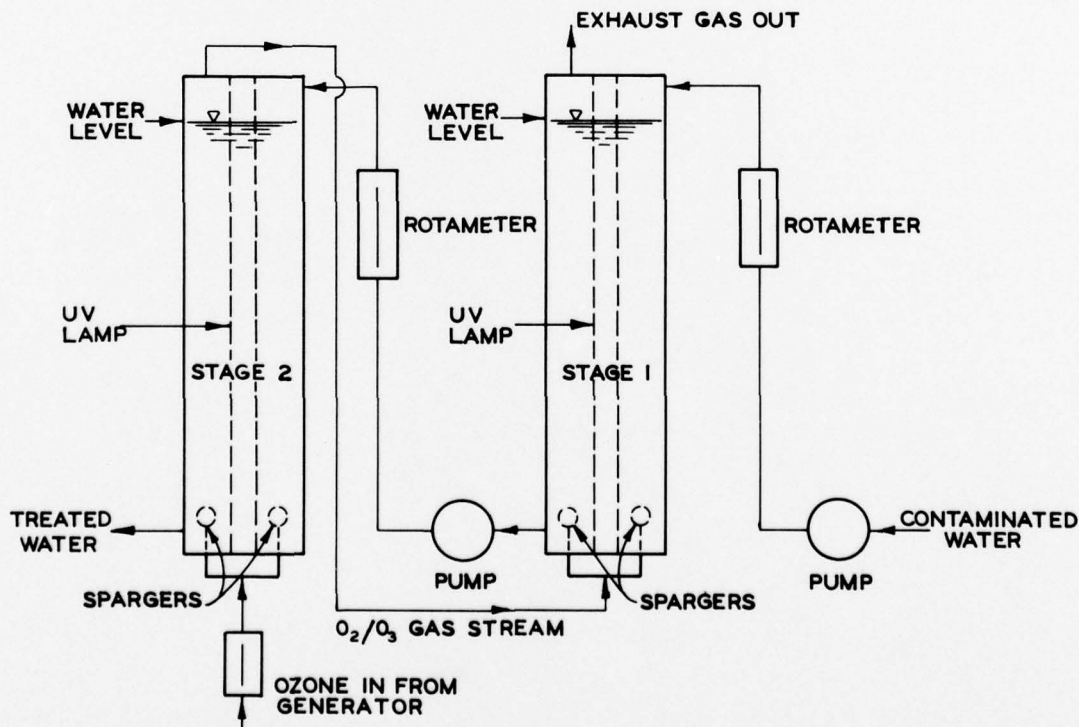


Figure 5. Schematic diagram of continuous flow bench system

an  $O_2/O_3$  mixture was introduced into stage two. The exhaust gas from stage two (containing the unreacted ozone) was passed into stage one. After bubbling through the incoming feedwater, this gas was exhausted from the system through the top of the stage one reactor. Continuous flow of feedwater was achieved by actuating the metering pumps to stages one and two and by opening the drain valve on stage two. The flow rate of the feedwater was then adjusted to allow sufficient contact time for the TOC of the effluent from stage two to be reduced to approximately 5 ppm. The system was allowed to operate until steady-state conditions were established, and then samples were taken for analysis.

### PART III: RESULTS

#### TOC Removal

15. TOC removal was used in this study as an indication of the destruction of organic contaminants. It should be noted that TOC measurements include all forms of organic carbon. For example, in a TOC measurement, DCPD is not distinguishable from its decomposition products unless the DCPD decomposes completely to  $\text{CO}_2$ . For this reason, TOC removal cannot be directly correlated with toxic organic removal, except that complete TOC removal would indicate total destruction of all organics.

16. Table 6 presents the results of the batch tests using reactor A, and Figures 6 and 7 show graphically the percent TOC removal. The maximum percent TOC removal (66) for a 120-min contact time occurred when the maximum UV power input and  $\text{O}_3$  mass flow were used, although with the reactor in this configuration, the UV power input does not appear to control the reaction. Experimental runs 3 and 9 were made with similar  $\text{O}_3$  mass flow rates and similar initial TOC levels. The runs resulted in nearly identical final TOC levels after 120 min, although runs 9 and 3 had a 43- and 28-w UV power input, respectively. The design of reactor A did not permit measurement or control of the reaction temperature.

17. Table 7 lists the results of batch tests using reactor B, and Figures 8 and 9 show graphically the percent TOC removal. The maximum percent TOC removal (90) for a 120-min contact time was obtained when the reactor was run using the following parameters:

UV power input	= 100 w
$\text{O}_3$ mass flow rate	= 86.9 mg/min
$\text{O}_2 + \text{O}_3$ gas flow rate	= 3.0 l/min
$\text{O}_3$ concentration	= 2.01 percent by weight (wt %)
Temperature	= 60°C

The highest percent TOC removals (runs 16, 17, and 18) are associated

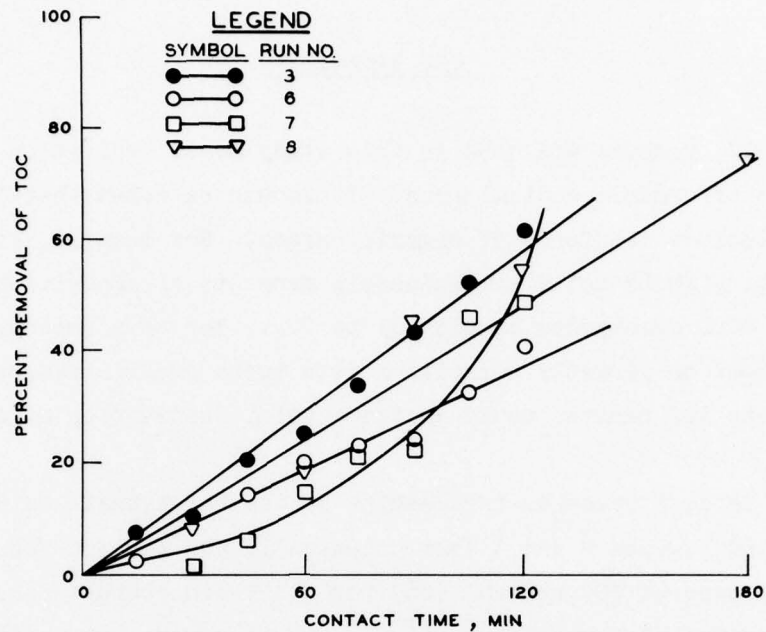


Figure 6. Percent TOC removal with reactor A using 28-w UV power input

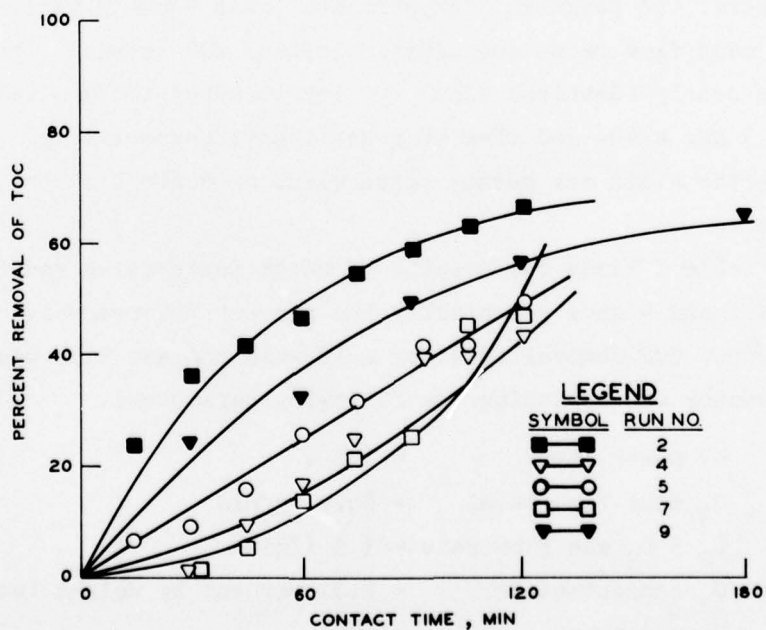


Figure 7. Percent TOC removal with reactor A using 43-w UV power input



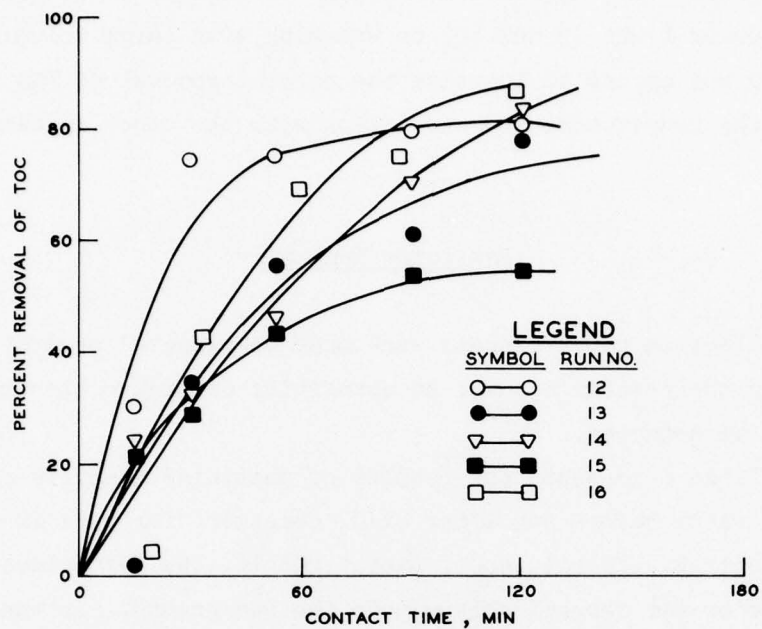


Figure 8. Percent TOC removal using reactor B, 100-w and control (lamp-off) runs

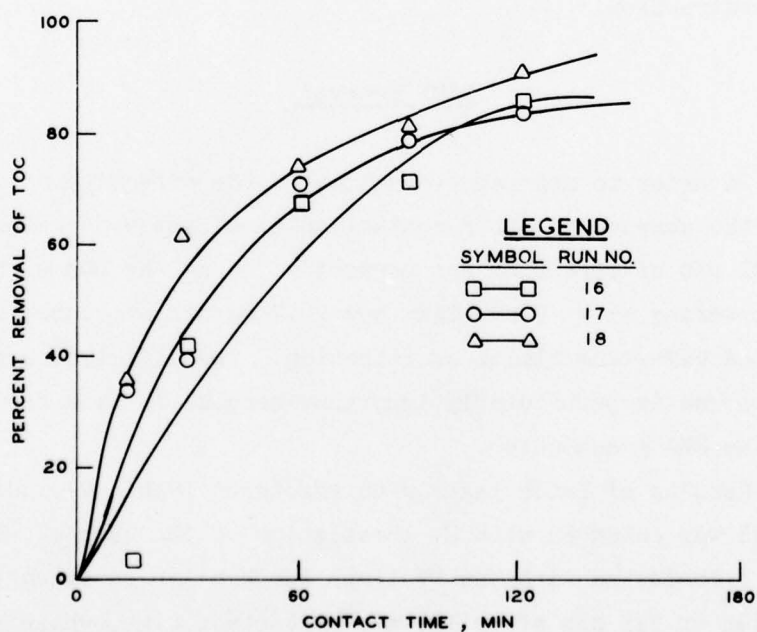


Figure 9. Percent TOC removal using reactor B, 200- and 400-w runs

with the highest temperatures. The design of reactor B was such that raising UV power (runs 13 and 14) or sparging with large volumes of gas (run 15) did not appear to increase the percent removal of TOC as much as raising the temperature in association with the other experimental variables.

#### Pesticide Removal

18. Electron capture scans were made on selected product water samples from the reactor A runs; no quantities of organochlorine pesticides could be detected.

19. Table 8 presents the results of pesticide analysis of feed and product water before and after UV/O<sub>3</sub> treatment for runs 12 through 18 with reactor B. In all cases, except run 16, the pesticides were undetectable or not recognizable within the background. In run 16, the endrin level remained at 0.1 ppb. In this experiment, no UV lamp was used. This run indicates the importance of UV radiation in assuring pesticide destruction.

#### DIMP Removal

20. In order to make an evaluation of the effectiveness of DIMP removal in the absence of other contaminants, a sample of water containing 2181 ppb of pure DIMP was prepared. In a 2-hr run with reactor A delivering 43 w of UV light and 20.7 mg/min of ozone, the DIMP level dropped below the limits of detection. The efficient destruction of this compound is particularly important because it is a major pollutant in the RMA groundwater.

21. Results of batch tests with reactor A (Table 9) indicate that DIMP removal was enhanced with UV irradiation of the sample. Experimental run 7 conducted with the UV lamps inoperative resulted in a DIMP concentration of 533 ppb after 120 min of contact time, while all runs performed with UV lamps in operation resulted in much lower DIMP concentrations in the product water. The results also indicated that the

increase in UV power from 28 to 43 w did not significantly effect DIMP removal. The greatest DIMP removal was associated with the experimental runs with the longest contact times. Among the experimental runs with identical contact times, the greatest DIMP removal was associated with the highest  $O_3$  mass flow rate.

22. The results from experimental runs using reactor B (Table 10) indicated that the concentration of DIMP could be lowered below the detection limit within a 2-hr contact time. Figure 10 shows the percent

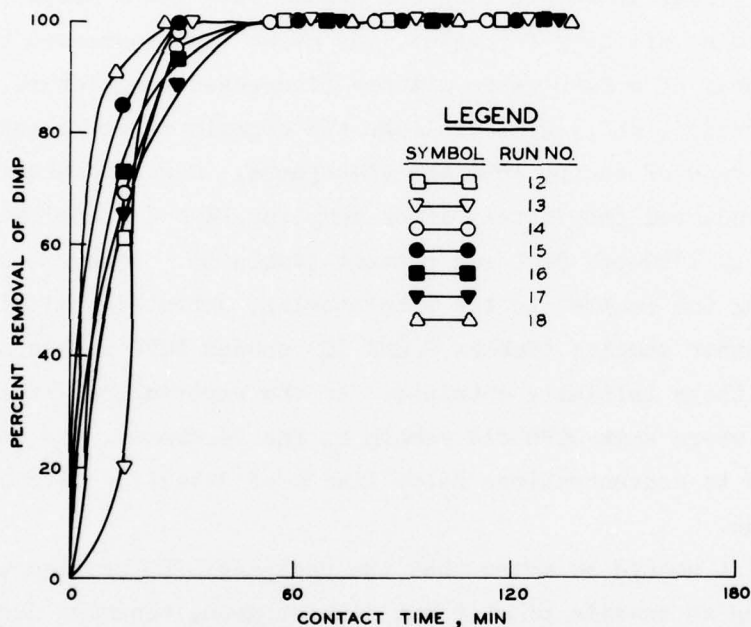


Figure 10. Percent DIMP removal using reactor B

DIMP removal using reactor B. The design of the experiment using reactor B allows for greater UV radiation and ozone concentrations resulting in more efficient removal of DIMP than in reactor A experiments. With the long contact time and high  $O_3$  mass flow rates coupled with effective mixing in reactor B, low levels of DIMP could be attained even without UV radiation (experimental run 16). With the data obtained from reactors A and B, nearly complete DIMP removal can be achieved with shorter contact times (<120 min) by optimizing the UV/ $O_3$  flow/temperature relationship.

### DCPD Removal

23. Due to its molecular structure, DCPD is extremely vulnerable to photochemical oxidative destruction. The UV/O<sub>3</sub> treatment is probably one of the best available processes to effect complete removal of DCPD from contaminated water. However, the experimental results (Tables 9 and 10) offer little confirming evidence. DCPD is less dense than water and extremely volatile. The compound dispersed in water will, on standing, rise to the surface and escape into the atmosphere. Since it has no affinity for water, any event that increases the kinetic energy of a DCPD water mixture (increased temperature, agitation, aeration, etc.) will dislodge the organic molecule and increase its rate of escape into the atmosphere. Gas chromatographic analysis conducted immediately after sampling PW No. 2 indicated that approximately 1000-ppb DCPD was present (Table 3). However, after transporting the samples to the laboratories, repeated analysis of UV/O<sub>3</sub> feedwater samples (Tables 9 and 10) showed DCPD levels much lower than those initially obtained. In the experimental runs using reactor B, where some DCPD did remain in the feedwater, the compound was reduced to concentrations below limits of detection with a 2-hr contact time.

24. It should be noted that the escaping DCPD problem would not occur during an on-site pilot plant test program, assuming direct pumping of contaminated water to the UV/O<sub>3</sub> unit. In a multistage UV/O<sub>3</sub> treatment unit, it is unlikely that DCPD would be swept from solution unless an extremely high O<sub>3</sub> mass flow was used.

25. On a calibration run with reactor A, a sample with a large quantity of low-density organics was skimmed from the feedwater prior to mixing. An analysis of this water showed an initial TOC of 21 mg/l. The sample was placed into the reactor and the experimental run conducted with a UV power input of 43 w and an O<sub>3</sub> mass flow rate of 64 mg/min. At the end of a 180-min contact time, the TOC level dropped to 2.4 mg/l, which represents an 89 percent removal of TOC.



### Continuous Flow Experiments

26. A series of continuous flow experimental runs were made using a two-stage reactor. Table 11 presents the operating parameters and resulting TOC values for the experimental runs. The maximum percent TOC removal (67) was obtained in experimental run 25 with a contact time of 150 min per stage, an  $O_3$  mass flow rate of 25.5 mg/min, and a UV power input of 43 w. Run 25 represents one of the longest contact times used coupled with the maximum ozone and UV power used in the type A reactors. Having a longer contact time but a lower rate of ozone flow, run 24 showed a lower TOC removal. This suggests that ozone levels, not contact times, were controlling the efficiency of TOC removal in the two-stage continuous flow system. It should be noted that the bench reactors used for the continuous flow studies do not contain any internal baffles or stirrers. Thus, this could possibly allow flow of influent to the outlet without adequate contact time. Improving the design of the reaction chambers might significantly increase the TOC removal rate in the continuous flow system.

27. Table 12 presents the results of analysis for selected organic contaminants for effluent from four experimental runs using the two-stage continuous flow reactor. Analyses were made for p-chlorophenylmethyl-(sulfide, sulfoxide, and sulfone), DIMP, and DCPD. The effluent water analysis showed that concentrations of all these contaminants were below limits of detection (<10 ppb) except for DIMP. These data indicate that experimental run 25 resulted in the greatest DIMP removal. The comparison of operating parameters indicated that the lowest DIMP concentrations in the effluent are associated with runs having high-UV power input and high ozone mass flow rates. In the continuous flow experiments, the effluent water was also tested for pesticides; no quantities of pesticides could be detected.

### Precipitation of Inorganic Materials

28. In both batch and continuous flow systems, a small amount of

precipitate was observed to form during each experimental run. Analysis performed on the product water and the precipitate indicated that the precipitate was largely iron oxide-hydroxides.

#### PART IV: CONCLUSIONS AND RECOMMENDATIONS

##### Conclusions

29. On the basis of data generated in this preliminary treatability study on RMA groundwater using two designs of laboratory-scale UV/O<sub>3</sub> reactors, it can be tentatively concluded that:

- a. The applicability of the UV/O<sub>3</sub> process to the treatment of water contaminated with organic compounds was successfully demonstrated. Concentrations of contaminating organic compounds identified in this study were reduced significantly (below detection limits in most cases) by this treatment process.
- b. As might be expected, elevated temperature accelerated the rate of reaction in the treatment process. The UV radiation appeared to aid in the disappearance of DIMP based on the results from reactor A. The gain in efficiency in removal of organics due to increases in the O<sub>3</sub> mass flow rate depended on the experimental design. Predictably, the percent removal of organic contaminants increased with increasing contact time. Successful performance of any reactor is related to optimizing these four important operating parameters.
- c. Percent TOC removal in the batch testing phase of the study ranged from 40 to 90 percent. The concentrations of the pesticides and other organic contaminants except for DIMP were reduced to below detectable limits.
- d. The data generated in the continuous flow phase of this study indicated that the levels of contaminating organic compounds could be significantly lowered using reactors in this configuration. With selected operating parameters, it was possible to lower the level of pesticides, DCPD, and organic sulfur compounds below the limit of detection (<10 ppb) and to remove 93 percent of the DIMP originally present in the sample.
- e. A precipitate presumed to be iron oxide-hydroxide was observed to form during all reactions.

##### Recommendations

30. Based on information gathered in the treatability study on RMA groundwater using bench-scale UV/O<sub>3</sub> reactors, the following recommendations can be made:

- a. Additional bench-scale work should be undertaken to more clearly identify optimum operating conditions. Such additional work should include modification or redesign of existing reactors to allow the investigation of new parameters, such as elevated temperatures, elevated pressures, and mechanical mixing rates.
- b. Existing small UV/O<sub>3</sub> pilot plants are sufficiently flexible in design to allow an immediate pilot study to be undertaken. As suggested equipment modifications and/or changes in operating parameters become available from the ongoing bench-scale work, they can be evaluated and included in a pilot plant system. Therefore, a flexible pilot system (5 gpm) should be obtained and installed at RMA.
- c. Future investigations, either bench or pilot scale, should include analysis of exhaust gases from each reactor to determine loss of unreacted volatile organics, ozone consumption, and decomposition products.
- d. Feedwater, product water, and precipitates from both bench- and pilot-scale reactors should be analyzed for trace metals to determine if trace metal contaminants are being removed in the ozonization process.



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Table 1  
Pesticides Subjected to UV/O<sub>3</sub> Photochemical Oxidation  
in MERADCOM Study<sup>3</sup>

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Malathion	(organophosphorus compound)
Baygon	(carbamate)
Vapam	(thiocarbamate)
Pentachlorophenol	
DDT	

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Table 2  
Organic Contaminants Identified in  
RMA Groundwater

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Aldrin
Dieldrin
Dicyclopentadiene
Diisopropylmethylphosphonate
Endrin
p-Chlorophenylmethylsulfide
p-Chlorophenylmethlysulfoxide
p-Chlorophenylmethylsulfone

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Table 3  
Organic Contaminants in RMA Test Samples\*

<u>Compound</u>	<u>PW No. 2</u>	<u>PW No. 3</u>
Aldrin	<2	<2
Dieldrin	4.5	<2
Dicyclopentadiene	800 1200	80 84
Diisopropylmethylphosphonate	410 400 780	3600 1800 3000
p-Chlorophenylmethyl-		
sulfide	68.3	<10
sulfoxide	53.3	<10
sulfone	40.5	<10
Endrin	8.6	<2
Nemagon	8.5 6.6	<1

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\* All values expressed as ppb.

Table 4  
General Water-Quality Parameters for RMA Test Samples\*

Parameter	PW No. 2	PW No. 3
Total Kjeldahl nitrogen	2.50	1.95
Nitrite nitrogen	<0.010	<0.010
Nitrate nitrogen	<0.010	0.012
Ammonia nitrogen	<0.010	<0.010
Total phosphorus	1.84	0.94
(essentially all organic phosphorus)	1.33	0.70
Phosphate phosphorus	<0.01	<0.01
Total organic carbon	20.0	10.0
	10.7	8.3
	8.3	8.0
Total inorganic carbon	68	74
Sulfate	270	810
	250	765
	210	725
Chloride	350	580
	330	525
	280	460
pH	7.77	7.56
	7.69	7.53
Chemical oxygen demand (COD)	26.3	22.9
Suspended solids	8.3	12.5
Total solids	1218.5	2439.8

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\* All values expressed as ppm except pH.



Table 5  
Metals in RMA Test Samples\*

<u>Metal</u>	<u>PW No. 2</u>	<u>PW No. 3</u>
Aluminum	0.101	0.146
Arsenic	0.008	0.013
Barium	0.1	0.1
Boron	0.478	0.771
Beryllium	0.008	0.006
Calcium	90.2	237.0
Cadmium	0.002	0.008
Cobalt	0.1	0.1
Chromium	0.009	0.016
Copper	0.001	0.001
Iron	0.022	0.159
Lead	0.001	0.001
Magnesium	49.0	59.9
Manganese	1.63	0.444
Molybdenum	0.127	0.1
Nickel	0.042	0.021
Potassium	4.14	9.52
Selenium	0.003	0.003
Sodium	243.0	508.0
Zinc	0.030	0.017
Mercury	0.0002	0.0002

---

\* All values expressed as ppm.

Table 6  
Operating Parameters and TOC Levels Obtained Using Reactor A

Operating Parameters															
Run No.	UV Power Input watts	O <sub>3</sub>		O <sub>3</sub> Conc wt %	TOC Remaining After Indicated Contact Times, ppm										
		Mass Flow Rate mg/min	O <sub>2</sub> + O <sub>3</sub> Gas Flow Rate l/min		0 min	15 min	30 min	45 min	60 min	75 min	90 min	105 min	120 min	180 min	
7	0	18.0	0.6	2.1	8.0	--	8	7.6	6.9	6.3	6.1	4.4	4.2		
6	28	16.5	0.8	1.4	9.0	8.8	8.2	7.8	7.3	7.0	6.9	6.1	5.4		
8	28	20.0	0.7	2.1	9.3	--	8.5	--	7.5	--	5.2	--	4.3	2.4	
3	28	20.7	0.7	2.05	10.0	9.3	9.0	8.0	7.6	6.7	5.7	4.8	3.9		
5	43	16.0	0.9	1.2	9.0	8.4	8.2	7.6	6.7	6.2	5.6	5.3	4.6		
9	43	20.7	0.7	2.2	9.6	--	7.3	--	6.5	--	4.9	--	4.2	3.4	
4	43	21.1	0.7	1.9	7.9	--	7.9	7.2	6.7	6.0	4.9	4.7	4.5		
2	43	29.0	0.9	2.3	11.2	8.6	7.2	6.6	6.0	5.1	4.7	4.2	3.8		

Note: This model reactor has no temperature recording or regulating device.

Table 7

## Operating Parameters and TOC Levels Obtained Using Reactor B

Run No.	Operating Parameters										TOC Remaining After Indicated Contact Times, ppm						
	UV Power Input watts	O <sub>3</sub> Mass Flow Rate mg/min	O <sub>2</sub> + O <sub>3</sub> Gas Flow Rate l/min	O <sub>3</sub> Conc wt %	Temperature °C	0 min		15 min		30 min		60 min		90 min		120 min	
16	0	86.3	3.0	2.0	40	6.0	5.8	3.5	1.9	1.7	0.8						
17	100	30.0	1.0	2.1	60	7.5	4.9	4.5	2.2	1.6	1.0						
18	100	86.9	3.0	2.01	60	7.1	4.6	2.7	1.8	1.4	0.7						
12	200	57.9	2.0	2.01	24	9.8	6.8	2.5	2.4	2.0	1.8						
13	400	60.1	2.0	2.09	27	10.7	10.5	7.0	4.8	4.1	2.4						
14	400	61.0	2.0	2.12	50	11.5	8.9	7.7	6.3	3.4	2.0						
15	400	124.6	4.0	2.16	27	10.6	8.3	7.6	6.0	4.9	4.8						

Table 8  
Concentrations of Pesticides Before and After UV/Ozone Treatment Using Reactor B\*

Run No.	Aldrin		Dieldrin		Endrin	
	Feed	Product**	Feed	Product	Feed	Product
12	1.1	0.1	4.2	<0.04	6.8	<0.5
13	1.1	0.1	4.0	<0.04	6.7	<0.5
14	1.76	0.1	5.9	<0.04	1.8	<0.5
15	1.76	0.1	4.9	<0.04	1.8	<0.5
16	1.4	0.1	4.4	<0.04	6.6	0.1
17	1.3	0.1	4.0	<0.04	5.7	<0.05
18	1.4	0.1	4.2	<0.04	6.6	<0.05

\* All values expressed as ppb.

\*\* The persistence of aldrin in the product water may be due to a small amount of some other interfering component, which elutes at the same time on the gas chromatograph.



Table 9

Concentrations of Organic Contaminants Before and After UV/Ozone Treatment Using Reactor A\*

Run No.	p-Chlorophenylmethyl-											
	Sulfide		Sulfoxide		Sulfone		DIMP		DCPD			
	Feed	Product	Feed	Product	Feed	Product	Feed	Product	Feed	Product		
2	24.0	<10	53.3	<10	35.2	<10	2130	7.7	<10	--**		
3	--**	<10	53.3	<10	35.2	<10	2130	15.0	<10	--**		
4	--**	<10	53.3	<10	35.2	<10	2130	13.0	<10	--**		
5	--**	<10	53.3	<10	35.2	<10	2130	63.0	<10	--**		
6	--**	<10	53.3	<10	35.2	<10	2130	50.0	<10	--**		
7	--**	<10	53.3	<10	35.2	<10	2130	533.0	<10	--**		
8	31.4	<10	61.2	<10	40.2	<10	1830	<0.5	<10	--**		
9	32.7	<10	63.5	<10	44.3	<10	1820	<0.5	<10	--**		
10	23.2	<10	52.9	<10	47.6	<10	1910	<0.9	<10	--**		

\* All values expressed as ppb.

\*\* Analyses not performed.

Table 10  
Concentration of Organic Contaminants Before and After UV/Ozone Treatment Using Reactor B\*

Run No.	p-Chlorophenylmethyl-											
	Sulfide		Sulfoxide		Sulfone		DIMP		DCPD			
	Feed	Product	Feed	Product	Feed	Product	Feed	Product	Feed	Product	Feed	Product
12	32.5	<10	54.7	<10	40.2	<10	2200	<2	24.0	<10		
13	--**	<10	54.7	<10	40.2	<10	1800	<2	41.0	<10		
14	--**	<10	34.7	<10	40.2	<10	2600	<2	20.0	<10		
15	--**	<10	54.7	<10	40.2	<10	1800	<2	2.4	<10		
16	--**	<10	54.7	<10	40.2	<10	1182	<2	14.0	<10		
17	--**	<10	54.7	<10	40.2	<10	1093	<1	15.0	<10		
18	--**	<10	54.7	<10	40.2	<10	1494	<1	12.0	<10		

\* All values expressed as ppb.

\*\* Analyses not performed.

## Summary of Continuous-Flow Experiments

No.	Stage 1				Stage 2					
	Flow Rate ml/min	Contact Time per Reactor min	O <sub>3</sub> Conc wt %	O <sub>3</sub> Mass Flow Rate mg/min	UV Power Input watts	Effluent TOC mg/l	O <sub>3</sub> Conc wt %	O <sub>3</sub> Mass Flow mg/min	UV Power Input watts	Effluent TOC ppm
19	100	120	2.2	18.8	28	6.0	2.2	18.8	0	4.1
20	100	120	2.1	17.7	0	7.5	2.1	17.7	28	3.9
21	100	120	2.1	17.7	28	6.5	2.1	17.7	28	3.2
22	100	120	2.1	18.0	28	8.1	2.1	18.0	0	5.0
23	100	120	2.0	8.6	28	8.4	2.0	8.6	28	7.0
24	60	200	2.0	15.4	43	5.5	2.0	15.4	43	2.5
25	80	150	2.5	25.5	43	5.4	2.5	25.5	43	1.8

Note: TOC of feed water in all experiments averaged 9.6 mg/l. All runs at ambient temperature.

Table 12  
Concentrations of Organic Contaminants After UV/Ozone  
Treatment in a Continuous-Flow System\*

Run No.	<u>p-Chlorophenylmethyl-</u>			<u>DIMP</u>	<u>DCPD</u>
	<u>Sulfide</u>	<u>Sulfoxide</u>	<u>Sulfone</u>		
19	<10	<10	<10	460.0	<10
21	<10	<10	<10	312.0	<10
24	<10	<10	<10	110.0	<10
25	<10	<10	<10	43.8	<10

\* All values expressed as ppb.



APPENDIX A: SURFACE WATER CRITERIA FOR PUBLIC WATER SUPPLIES\*

Constituent or Characteristic	Permissible Criteria mg/l	Desirable Criteria mg/l
Inorganic chemicals:		
Ammonia	0.5 (as N)	<0.01
Arsenic	0.05	Absent
Barium	1.0	do
Boron	1.0	do
Cadmium	0.01	do
Chloride	250	<25
Chromium, hexavalent	0.05	Absent
Copper	1.0	Virtually absent
Dissolved oxygen	>4 (monthly mean) >3 (individual sample)	Near saturation
Fluoride	<2.4	<1.4
Iron (filterable)	0.3	Virtually absent
Lead	0.05	Absent
Manganese (filterable)	0.05	do
Nitrates plus nitrites ph (range)	10 (as N) 6.0-8.5	Virtually absent
Selenium	0.01	Absent
Silver	0.05	do
Sulfate	250	<50
Total dissolved solids (filterable residue)	500	<200
Uranyl ion	5	Absent
Zinc	5	Virtually absent
Organic chemicals:		
Carbon chloroform extract (CCE)	0.15	<0.04
Cyanide	0.20	Absent
Methylene blue active substances	0.5	Virtually absent
Oil and grease	Virtually absent	Absent
Pesticides:		
Aldrin	0.017	do
Chlordane	0.003	do
DDT	0.042	do
Dieldrin	0.017	do
Endrin	0.001	do

\* Water-Quality Criteria, report of the National Technical Advisory Committee to the Secretary of the Interior, April 1, 1968 (reprinted by EPA in 1972).

Constituent or Characteristic	Permissible Criteria mg/l	Desirable Criteria mg/l
Heptachlor	0.018	do
Heptachlor epoxide	0.018	do
Lindane	0.056	do
Methoxychlor	0.035	do
Organic phosphates plus carbamates	0.1	do
Toxaphene	0.005	do
Herbicides	0.005	do
2,4-D plus 2,4, 5-T, plus 2,4, 5-TP	0.1	do
Phenols	0.01	do
Radioactivity:	(pc/l)	(pc/l)
Gross beta	1000	<100
Radium-226	3	<1
Strontium-90	10	<2

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Evaluation of ultraviolet/ozone treatment of Rocky Mountain Arsenal (RMA) groundwater (treatability study) / by Robert E. Buhts, Philip G. Malone, Douglas W. Thompson. Vicksburg, Miss. : U. S. Waterways Experiment Station ; Springfield, Va. : available from National Technical Information Service, 1978.

25, 210, 2 p. : ill. ; 27 cm. (Technical report - U. S. Army Engineer Waterways Experiment Station ; Y-78-1)

Prepared for the Project Manager for Chemical Demilitarization and Installation Restoration, Aberdeen Proving Ground, Maryland.

References: p. 25.

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